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(54) **Heat-resistant support for catalysts and the production thereof**

Hitzebeständiger Träger für Katalysatoren und deren Herstellung

Support résistant à la chaleur pour catalyseurs et leur production

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(73) Proprietor: **TOYOTA JIDOSHA KABUSHIKI**
KAISHA
Aichi-ken 471-8571 (JP)

(72) Inventors:

- **Yoshida, Takeru**
Toyota-shi, Aichi-ken (JP)
- **Murachi, Mikio**
Toyota-shi, Aichi-ken (JP)
- **Tsuji, Shinji**
Toyota-shi, Aichi-ken (JP)

- **Taguchi, Norio**
Toyota-shi, Aichi-ken (JP)

(74) Representative:
Winter, Brandl, Fürniss, Hübner, Röss, Kaiser,
Polte Partnerschaft
Patent- und Rechtsanwaltskanzlei
Alois-Steinecker-Strasse 22
85354 Freising (DE)

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EP 0 718 028 B1

Description

BACKGROUND OF THE INVENTION5 Field of the Invention

[0001] This invention relates to a high heat-resistant catalyst support used for a catalyst for purifying automotive exhaust gases and the like, a method of producing the catalyst support at a low cost, a high heat-resistant catalyst using the catalyst support, and its production methods, according to claims 1 to 3.

10 Description of Related Art

[0002] As catalysts for purifying automotive exhaust gases, there have been employed 3-way catalysts so far which oxidize carbon monoxide (CO) and hydrocarbons (HC) and reduce nitrogen oxides (NO_x) to purify the exhaust gases. For example, the 3-way catalysts have been known widely which comprise a heat-resistant supporting base material formed of cordierite, a porous catalyst support layer formed of gamma-alumina and disposed on the supporting base material, and a noble metal catalyst ingredient such as platinum (Pt) and rhodium (Rh) loaded on the porous catalyst support layer. Further, the 3-way catalysts are also known in which ceria i.e., cerium oxide having an oxygen storage ability is employed in addition to the above catalyst ingredient in order to improve catalytic activity at low temperatures.

[0003] In the meanwhile, carbon dioxide (CO₂) in exhaust gases from internal combustion engines of automobiles and the like has become a problem in view of global environmental conservation. Lean burn in oxygen excessive atmospheres is desired as a means of dissolving the problem. The lean burn improves fuel consumption, and as a result the amount of fuel used is decreased and CO₂, which is included in combustion exhaust gas, can be suppressed from generating.

[0004] In this respect, the conventional 3-way catalysts aim to oxidize CO and HC and reduce NO_x simultaneously into innocuous entities when the air-fuel ratio is at the stoichiometric point (or the ideal air-fuel ratio), and cannot exhibit sufficient reduction and removal of NO_x in the exhaust gases which contain oxygen in excessive amounts required for oxidizing carbon monoxide and hydrocarbons therein at the time of lean burn. Hence, it has been desired to develop catalysts and exhaust gas purifying systems which are capable of adequately purifying NO_x even in oxygen excessive atmospheres.

[0005] In view of the aforementioned circumstances, the applicants et al of the present invention have proposed an exhaust gas purifying catalyst in which alkaline-earth metals and platinum (Pt) are loaded on a porous support formed of alumina and the like in Japanese Unexamined Patent Publication (KOKAI) No.5-317,652, an exhaust gas purifying catalyst in which lanthanum (La) and platinum (Pt) are loaded on a porous support in Japanese Unexamined Patent Publication (KOKAI) No.5-168,860, and an exhaust gas purifying catalyst in which alkali metals and platinum (Pt) are loaded on an alumina support in Japanese Unexamined Patent Publication (KOKAI) No.6-31,139. In using these catalysts, NO_x are adsorbed on oxides of alkaline-earth metals or lanthanum oxide on the fuel-lean side (i.e., in the oxygen excessive atmospheres), and the adsorbed NO_x react with reducing components such as HC and CO at the stoichiometric point or on the fuel-rich side (i.e., in the oxygen-lean atmospheres). So, these catalysts attain excellent NO_x purifying performance even on the fuel-lean side.

[0006] The production of these catalysts is mainly achieved by what we call a loading-by-water absorption method. For example, first, a porous support formed of alumina or the like is impregnated with a solution containing a chemical compound of a noble metal catalyst ingredient, dried, and calcined, thereby loading the noble metal catalyst ingredient thereon. Second, the noble metal-loaded support is reimpregnated with a solution containing a chemical compound of an NO_x storage component, dried, and calcined, thereby loading the NO_x storage component thereon.

[0007] By the way, the average temperature and the maximum temperature of inlet gases to the bed of catalysts tend to rise more and more in recent years due to severe restrictions on exhaust gases and the improvement in the capacity of engines. Therefore, it is desired to make a further improvement in the heat resistance of catalysts for purifying exhaust gases. Further, with an increase in inlet gas temperatures, it is also desired to improve NO_x conversion at elevated temperatures.

[0008] In the conventional catalysts, however, there arises a problem that NO_x storage components react with catalyst supports at high temperatures and as a result the NO_x storage ability of the NO_x storage components is deteriorated. Besides, in the conventional catalysts, a temperature range in which the maximum catalyst performance is obtained, namely, a temperature window is narrow, and the NO_x conversion is hardly secured at elevated temperatures.

[0009] Further, in the conventional catalysts, the NO_x storage components are poisoned by SO_x which are produced from a very small amount of sulfur contained in fuel, in other words, the NO_x storage ability is decreased due to sulfate generation. Consequently, the catalysts are degraded in durability.

[0010] Further, in the conventional methods of producing catalysts, the NO_x storage components are loaded by a

loading-by-water absorption method. When this method is employed, the NO_x storage components have a poor dispersion, i.e., a maldistribution. As a result, crystallization of the NO_x storage components is promoted at and around a part having a high loading concentration of the NO_x storage components, so that the NO_x storage ability is deteriorated. The NO_x storage ability, especially at elevated temperatures is greatly influenced by the combination of NO_x storage components and catalyst supports, and the dispersibility of NO_x storage components.

[0011] Further, when the NO_x storage components are poorly dispersed, sulfate crystals generated by sulfur poisoning easily grow and therefore, become more difficult to be removed, so that the durability of the catalysts is decreased. In addition, in the case where the NO_x storage component is an alkali metal, the NO_x storage component tends to be flown away or eluted by water vapor contained in exhaust gases, because the NO_x storage component is loaded on the surface of the catalyst support in the conventional methods. Hence, the catalyst is poor in durability.

[0012] GB-A-2 248 194 discloses a catalyst for cleaning exhaust gases the support of which is not disclosed as being an amorphous composite oxide. JP-A-04 363 138 discloses a catalyst comprising clay mineral with double chain crystal structure.

SUMMARY OF THE INVENTION

[0013] The present invention has been developed in view of the aforementioned circumstances. It is therefore an object of the present invention to improve heat resistance and durability of a catalyst by highly dispersing an NO_x storage component.

[0014] A high heat-resistant catalyst support according to the present invention, which dissolves the above problems, comprises:

alumina, and

an NO_x storage component consisting of cesium oxide, wherein a part of said cesium oxide in the following formula (1) may be replaced with an oxide of at least one element selected from the group consisting of alkali metals except cesium, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper,

said alumina and said NO_x storage component constituting an amorphous composite oxide,

wherein said alumina and said NO_x storage component have a molar ratio satisfying the following formula (1):

$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1 / 90 \quad (1),$$

and

said amorphous composite oxide is an amorphous composition which has been subjected to a thermal treatment at a temperature at which said composition is not crystallized.

[0015] In the high heat-resistant catalyst support of the present invention, the NO_x storage component constitutes an amorphous composite oxide together with an oxide of aluminum, and highly dispersed. Therefore, the NO_x storage component is suppressed from reacting with a catalyst support, and heat resistance is secured. Further, even when sulfur poisoning is caused, sulfates are suppressed from growing owing to the high dispersion of the NO_x storage component. Since SO_x can be easily removed, the durability of the NO_x storage ability is superior.

[0016] In the catalyst support of the present invention, alumina is employed as the oxide, and cesium (Cs) is employed as an element constituting the NO_x storage component. Therefore, in addition to the fact that the same functions as that of the above basic catalyst support are exhibited, cesium is not only superior in NO_x storage ability at low temperatures, but also superior in NO_x storage ability at temperatures of 400°C or more because of interaction with aluminum.

[0017] This cesium is a strong base and firmly bonded with acidic NO_x, so the NO_x storage ability is excellent. Besides, since cesium more hardly reacts with alumina than barium and the like, the NO_x storage ability can be maintained high for a long time. Further, because cesium forms a composite oxide together with alumina in this catalyst support, a high durability is obtained. Even when sulfur poisoning is caused, sulfate is generated in the form of a composite sulfate of cesium and aluminum, and accordingly the sulfate is easily decomposable and removable than the sulfate of barium and the like.

[0018] The compositional molar ratio of cesium to aluminum satisfies the following formula:

$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1/90.$$

When a larger amount of cesium is contained, i.e., the ratio of Cs_2O to Al_2O_3 is equal to or more than $1/3$, although the catalyst support has an NO_x adsorbing ability, the release of NO_x in the reducing atmospheres is insufficient, the specific surface area is small, and heat resistance is deteriorated. On the other hand, when a smaller amount of cesium is contained, i.e., the ratio of Cs_2O to Al_2O_3 is equal to or less than $1/90$, the catalyst support is sintered at elevated temperatures, with the result that the specific surface area is lowered and necessary NO_x storage ability is hardly maintained. Therefore, the compositional ratio in this range achieves sufficient heat resistance and durability.

[0019] In the high heat-resistant catalyst support of the present invention, a part of the cesium may be replaced with at least one element selected from the group consisting of alkali metals except cesium, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper.

[0020] The replacing elements are superior in sulfur poison resistance to cesium. Therefore, both excellent NO_x purifying ability and sulfur poison resistance can be attained. For example, since titanium is an acidic element, sulfates are prevented from generating. Potassium or calcium forms a composite sulfate of three-element components together with cesium and aluminum. This sulfate can be decomposed at lower temperatures than composite sulfates of two-element components, so the decomposing temperature is lowered.

[0021] A method of producing a high heat-resistant catalyst support according to the present invention, comprises the steps of:

mixing a solution of a cesium compound which may include one further element selected from the group consisting of alkali metals, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper, with a solution of alumina sol to prepare a mixed sol solution,

forming said mixed sol solution into gel, and drying and calcining said gel.

[0022] In this production method, a solution of an NO_x storage component is mixed with a solution of oxide sol, and then dried and calcined. The oxide sol comprises fine particles having a specific surface area of approximately $500 \text{ m}^2/\text{g}$ or more, and the NO_x storage component is dispersed on the surface of these fine particles. Therefore, the NO_x storage component is dispersed very highly. Further, sufficient durability against elevated temperatures is maintained on account of high crystallizing temperature.

[0023] It must be noted that the NO_x storage component can be dispersed as highly as in this method, by supplying both of the metal oxide and the NO_x storage component in the forms of metal alkoxide and conducting a sol-gel method. In the sol-gel method, however, the costs of raw materials are quite high. The method of the present invention achieves production at a cost of $1/30$ or less based on the sol-gel method.

[0024] A high heat-resistant catalyst of the present invention, comprises:

a high heat-resistant catalyst support comprising an amorphous composition comprising alumina and an NO_x storage component consisting of cesium oxide, wherein a part of said cesium oxide in the following formula (1) may be replaced with an oxide of at least one element selected from the group consisting of alkali metals except cesium, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper, in which cesium oxide and alumina have a molar ratio satisfying the following formula (1):

$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1/90 \quad (1),$$

and which has been subjected to a thermal treatment at a temperature at which said composition is not crystallized; and

a porous support loaded with a noble metal.

[0025] The high heat-resistant catalyst of the present invention comprises the high heat-resistant catalyst support of the present invention and a noble metal-loaded porous support comprising a porous oxide loaded with a noble metal. The noble metal oxidizes NO in exhaust gases into NO_2 and make the NO_2 adsorbed by the highly dispersed NO_x storage component, while the noble metal reduces NO_x released from the NO_x storage component into innocuous N_2 .

[0026] In the high heat-resistant catalyst of the present invention, the porous support is preferably ceria.

[0027] In the method of the present invention, a noble metal is loaded on a porous support to prepare noble metal-loaded porous support powder, and then the noble metal-loaded porous support powder is mixed with the high heat-

resistant catalyst support of the present invention. This method prevents the NO_x storage component from eluting in contrast to the conventional platinum loading-by-water absorption method. Consequently, the NO_x storage component can secure a high dispersion. Thus, the method of the present invention can easily produce a catalyst which is superior in heat resistance and NO_x storage ability.

[0028] If a noble metal is loaded by the loading-by-water absorption method, when the catalyst support is immersed in a solution including a chemical compound of a noble metal, the NO_x storage component is eluted, which results in a decrease in the loading amount of the NO_x storage component. Further, because the eluted NO_x storage component aggregates on the surface of the catalyst support, the aggregated NO_x storage component reacts with the catalyst support, which results in a decrease in heat resistance.

[0029] In the method of producing a high heat-resistant catalyst of the present invention, the porous oxide constituting said support is preferably ceria.

[0030] When ceria i.e., cerium oxide is employed as a support comprising a high heat-resistant oxide in the catalyst of the present invention and its production method, since a noble metal is loaded on ceria beforehand, the above elution of the NO_x storage component is not observed. Further, owing to the oxygen storage ability of ceria, the variation in oxygen concentration is small in transitional areas from the stoichiometric point to the fuel-rich atmospheres or the fuel-lean atmospheres, whereby stable purifying performance is obtained.

[0031] In this catalyst of the present invention, since cesium is separated from a noble metal, it is possible to prevent inconveniences caused by the elution of cesium. Further, when cesium is disposed in the vicinity of a noble metal, the oxidation force of the noble metal is often reduced, which results in a decrease in HC conversion. In the present invention, however, since cesium is arranged at some distance from a noble metal, HC conversion can be prevented from decreasing.

[0032] Now, the present invention will be described more concretely.

(Catalyst Support)

[0033] The NO_x storage component may comprise at least one element selected from the group consisting of alkali metals except caesium, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper.

[0034] Examples of alkali metals are lithium, sodium, potassium, rubidium, and francium. Alkaline-earth metals are elements of group IIa in the periodic table and include barium, beryllium, magnesium, calcium, and strontium. Examples of rare-earth elements are scandium, yttrium, cerium, praseodymium, and neodymium.

[0035] The content of the NO_x storage component is preferably 1 to 50 mol based on 100 mol of the catalyst support material. When the content is less than 1 mol, the NO_x storage ability is small and the NO_x purifying performance is deteriorated. On the other hand, when the content exceeds 50 mol, the NO_x storage ability is saturated and at the same time there arises a problem that HC emission increases.

(Catalyst Support In Which A Part Of Cs Is Replaced)

[0036] The element replacing a part of cesium is at least one element selected from the group consisting of alkali metals, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper. Examples of such element is titanium (Ti), potassium (K) and calcium (Ca). When titanium is employed, since titanium is acidic, sulfate is hardly generated and sulfur poison resistance is enhanced. When potassium or calcium is employed, since it forms a composite sulfate of three-element components together with cesium and aluminum, this sulfate has a lower decomposing temperature than sulfates of two-element components, and is more easily removed.

(Method of Producing the Catalyst Support)

[0037] The solution of oxide sol is a aqueous solution of alumina sol.

[0038] It is preferable that the sol has a specific surface area of 200 m²/g or more. When the specific surface area is smaller than 200 m²/g, the dispersability of the NO_x storage component is lowered. The sol preferably has a concentration of 30 % by weight or less. When the sol concentration exceeds 30 % by weight, the dispersability of the sol is decreased and accordingly the heat resistance of the resulting catalyst support is degraded.

[0039] The mixing molar ratio of the chemical compound of at least one element selected from the group consisting of alkali metals, alkaline-earth metals, and rare-earth elements to the alumina sol lies in the range from 1 / 2 to 1 / 100, and preferably in the range from 1 / 3 to 1 / 12, when the chemical compound is converted into oxide. When the mixing molar ratio of the chemical compound is more than 1 / 2, the heat resistance is decreased due to a decrease in dispersibility of the NO_x storage component. When the mixing ratio of the chemical compound is less than 1 / 100, the NO_x storage ability is decreased and the NO_x purifying performance is degraded, although the heat resistance is not

lowered.

[0040] Examples of the above chemical compound are hydroxide, chloride, nitrate, and acetate, and aqueous solutions of these chemical compounds can be used.

[0041] As a method of mixing the oxide sol with the solution of the chemical compound, any known mixing method can be used such as ultrasonic wave radiation, an ultrasonic homogenizer, stirring, and a ball mill.

(Catalyst and Its Production Method)

[0042] The suitable mixing ratio of the noble metal-loaded porous support (powder) to the high heat-resistant catalyst support (powder) is 50 to 10 parts by weight of the noble metal-loaded porous support (powder) to 50 to 90 parts by weight of the high heat-resistant catalyst support (powder). When the high heat-resistant catalyst support (powder) is less than 50 parts by weight, the NO_x storage ability is lowered.

[0043] Now, advantages of the present invention will be described hereinafter.

[0044] According to the high heat-resistant catalyst support, since the NO_x storage component is highly dispersed, the NO_x storage component is suppressed from crystallizing, and high heat resistance is obtained.

[0045] According to the method of producing the high heat-resistant catalyst support, it is possible to stably and easily produce a catalyst support which is amorphous, which has a specific surface area of 100 m²/g or more even when calcined at temperatures of not less than 900°C, in which the NO_x storage component is highly dispersed, and which is superior in heat resistance.

[0046] According to the high heat-resistant catalyst, since the high heat-resistant catalyst support of the present invention is employed, high heat-resistance is obtained. According to the method of producing this high heat-resistant catalyst of the present invention, a metal catalyst ingredient is loaded on powder of an oxide such as cerium oxide beforehand, and then mixed with catalyst support powder. Therefore, the NO_x storage component is prevented from eluting and crystallizing. Consequently, the catalyst of the present invention attains a specific surface area of 100 m²/g or more even after a thermal treatment at 800°C, so high heat resistance is obtained.

[0047] Further, according to the method of producing a catalyst of the present invention, when the catalyst is used by being distended on a monolith support, the distention is achieved by a single coating, in contrast to a conventional case where the catalyst must be distended by a double or more coating. Thus, production steps can be reduced.

[0048] When ceria is employed as a porous support in the catalyst of the present invention and its production method, stable purifying performance can be obtained even in the transitional areas because of the oxygen adsorption and release function of ceria.

[0049] According to the high heat-resistant catalyst comprising:

a high heat-resistant catalyst support comprising an amorphous composition in which cesium oxide and aluminum oxide have a molar ratio satisfying the following formula:

$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1/90,$$

and which has been subjected to a thermal treatment at a temperature at which the composition is not crystallized; and a porous support loaded with a noble metal, the oxidation force of the noble metal catalyst ingredient is prevented from decreasing, and as a result, HC conversion is suppressed from decreasing, in addition to the fact that the advantages of the above catalyst are obtained.

PREFERRED EMBODIMENTS OF THE PRESENT INVENTION

[0050] The exact nature of this invention, as well as other objects and advantages thereof, will be readily apparent from consideration of the description of preferred embodiments of the present invention.

(A First Series of Preferred Embodiments Concerning a Catalyst Support)

Example 1

[0051] 27.8 g of cesium acetate and 118.5 g of aluminum triisopropoxide were dissolved in 450 ml of 2-propanol. After stirred with a reflux at 80°C for two hours, this solution was mixed with 14.5 g of 2,4-pentanedione, and further stirred for three hours. Then, while the solution was held at 80°C, a mixed solution of 67.9 ml of ion exchange water and 100 ml of 2-propanol was dropped into the solution. After stirred at 80°C for five hours, the resulting solution was vacuum dried to obtain white powder.

[0052] This powder was air calcined at 800°C for five hours, thereby preparing a catalyst support of Example 1. This catalyst support had a specific surface area of 68 m²/g. An X-ray diffraction analysis revealed that cesium and aluminum constituted an amorphous composite oxide, and that cesium was highly dispersed in aluminum. Cesium and aluminum were contained as oxides at a molar ratio of Cs₂O / Al₂O₃ = 1 / 4.

Example 2

[0053] A catalyst support of Example 2 was prepared in the same way as that of Example 1, with the exception of using 16.0 g of cesium acetate, 153.3 g of aluminum triisopropoxide, 580 ml in total of 2-propanol, and 84.0 ml of ion exchange water.

[0054] This catalyst support had a specific surface area of 161 m²/g. An X-ray diffraction analysis showed that cesium and aluminum constituted an amorphous composite oxide, and that cesium was highly dispersed in aluminum. Cesium and aluminum were contained as oxides at a molar ratio of Cs₂O / Al₂O₃ = 1 / 9.

Example 3

[0055] A catalyst support of Example 3 was prepared in the same way as that of Example 1, with the exception of using 13.7 g of cesium acetate, 160 g of aluminum triisopropoxide, 603 ml in total of 2-propanol, 17.1 g of 2,4-pentanedione, and 87.3 ml of ion exchange water.

[0056] This catalyst support had a specific surface area of 178 m²/g. An X-ray diffraction analysis indicated that cesium and aluminum constituted an amorphous composite oxide, and that cesium was highly dispersed in aluminum. Cesium and aluminum were contained as oxides at a molar ratio of Cs₂O / Al₂O₃ = 1 / 11.

Example 4

[0057] A catalyst support of Example 4 was prepared in the same way as that of Example 1, with the exception of using 7.6 g of cesium acetate, 178 g of aluminum triisopropoxide, 670 ml in total of 2-propanol, 18.2 g of 2,4-pentanedione, and 95.6 ml of ion exchange water.

[0058] This catalyst support had a specific surface area of 202 m²/g. An X-ray diffraction analysis proved that cesium and aluminum constituted an amorphous composite oxide, and that cesium was highly dispersed in aluminum. Cesium and aluminum were contained as oxides at a molar ratio of Cs₂O / Al₂O₃ = 1 / 22.

Example 5

[0059] A catalyst support of Example 5 was prepared in the same way as Example 1, with the exception of using 2.1 g of cesium acetate, 194.2 g of aluminum triisopropoxide, 731 ml in total of 2-propanol, 19.3 g of 2,4-pentanedione, and 103.2 ml of ion exchange water.

[0060] This catalyst support had a specific surface area of 227 m²/g. An X-ray diffraction analysis demonstrated that cesium and aluminum constituted an amorphous composite oxide, and that cesium was highly dispersed in aluminum. Cesium and aluminum were contained as oxides at a molar ratio of Cs₂O / Al₂O₃ = 1 / 88.

Comparative Example C6

[0061] A catalyst support of Example C6 was prepared in the same way as that of Example 1, with the exception of using 32.7 g of cesium acetate, 104.3 g of aluminum triisopropoxide, 495 ml in total of 2-propanol, 13.6 g of 2,4-pentanedione, and 61.3 ml of ion exchange water.

[0062] This catalyst support had a specific surface area of 8 m²/g. An X-ray diffraction analysis revealed that cesium and aluminum constituted an amorphous composite oxide. Cesium and aluminum were contained as oxides at a molar ratio of Cs₂O / Al₂O₃ = 1 / 3.

Comparative Example C7

[0063] A catalyst support of Example C7 was prepared in the same way as that of Example 1, with the exception of using 2.0 g of cesium acetate, 194.4 g of aluminum triisopropoxide, 731 ml in total of 2-propanol, 19.3 g of 2,4-pentanedione, and 103.3 ml of ion exchange water.

[0064] This catalyst support had a specific surface area of 230 m²/g. An X-ray diffraction analysis showed that cesium and aluminum constituted an amorphous composite oxide. Cesium and aluminum were contained as oxides at a molar ratio of Cs₂O / Al₂O₃ = 1 / 90.

Example 8

[0065] 11.1 g of cesium acetate, 1.4 g of calcium nitrate, and 160.1 g of aluminum triisopropoxide were dissolved in 600 ml of 2-propanol. After stirred with a reflux at 80°C for two hours, this solution was mixed with 17.1 g of 2,4-pentanedione and further stirred for three hours. Then, while this solution was held at 80°C, a mixed solution of 87.3 ml of ion exchange water and 100 ml of 2-propanol was dropped into the solution. After stirred at 80°C for five hours, the resulting solution was vacuum dried to obtain white powder.

[0066] This powder was air calcined at 800°C for five hours, thereby preparing a catalyst support of Example 8. This catalyst support had a specific surface area of 152 m²/g. An X-ray diffraction analysis indicated that cesium, calcium, and aluminum constituted an amorphous composite oxide, and that cesium and calcium were highly dispersed in aluminum. Cesium and calcium, and aluminum were contained as oxides at a molar ratio of (Cs₂O + CaO) / Al₂O₃ = 1 / 11.

Example 9

[0067] A catalyst support of Example 9 was prepared in the same way as that of Example 8, except that 4.0 g of titanium tetraisopropoxide was used instead of 1.4 g of calcium nitrate.

[0068] This catalyst support had a specific surface area of 148 m²/g. An X-ray diffraction analysis proved that cesium, titanium, and aluminum constituted an amorphous composite oxide, and that cesium and titanium were highly dispersed in aluminum. Cesium and titanium, and aluminum were contained as oxides at a molar ratio of (Cs₂O + TiO₂) / Al₂O₃ = 1 / 11.

Example 10

[0069] A catalyst support of Example 10 was prepared in the same way as Example 8, except that 1.4 g of potassium acetate was used instead of 1.4 g of calcium nitrate.

[0070] This catalyst support had a specific surface area of 157 m²/g. An X-ray diffraction analysis demonstrated that cesium, potassium, and aluminum constituted an amorphous composite oxide, and that cesium and potassium were highly dispersed in aluminum. Cesium and potassium, and aluminum were contained as oxides at a molar ratio of (Cs₂O + K₂O) / Al₂O₃ = 1 / 11.

Example 11

[0071] A catalyst support of Example 11 was prepared in the same way as that of Example 8, except that 2.9 g of lanthanum nitrate was used instead of 1.4 g of calcium nitrate.

[0072] This catalyst support had a specific surface area of 143 m²/g. An X-ray diffraction analysis revealed that cesium, lanthanum, and aluminum constituted an amorphous composite oxide, and that cesium and lanthanum were highly dispersed in aluminum. Cesium and lanthanum, and aluminum were contained as oxides at a molar ratio of (Cs₂O + La₂O₃) / Al₂O₃ = 1 / 11.

Comparative Example C12

[0073] 10.9 g of diisopropoxy barium and 104.3 g of aluminum triisopropoxide were dissolved in 430 ml of 2-propanol. After stirred with a reflux at 80°C for two hours, this solution was mixed with 16.6 g of 2,4-pentanedione and further stirred for three hours. While this solution was held at 80°C, a mixed solution of 58.3 ml of ion exchange water and 150 ml of 2-propanol was dropped into the solution. After stirred at 80°C for five hours, the resulting solution was vacuum dried to obtain white powder.

[0074] This powder was air calcined at 800°C for five hours, thereby preparing a catalyst support of Example C12. This catalyst support had a specific surface area of 235 m²/g. An X-ray diffraction analysis showed that barium and aluminum constituted an amorphous composite oxide, and that barium was highly dispersed in aluminum. Barium and aluminum were contained as oxides at a molar ratio of BaO / Al₂O₃ = 1 / 6.

Preparation of Catalysts

[0075] Catalyst support powder of each of the above examples was mixed at the ratio of 10 g of the catalyst support powder to 100 ml of a solution of platinum dinitrodiammine nitrate in 2-propanol containing platinum in an amount of 0.008 mol, and stirred at room temperature for one hour. Then, powder was separated by centrifugation, dried at 120°C for 12 hours, and subjected to a thermal treatment at 250°C for one hour, thereby loading platinum. The loading amount

of platinum was 1.12 % by weight.

[0076] 30 parts by weight of zirconia sol containing zirconia in an amount of 30 % by weight, and 400 ml of 2-propanol were added to 100 parts by weight of this Pt-loaded catalyst support powder, thereby preparing slurry. A honeycomb support formed of cordierite was immersed in this slurry, and then pulled up and blown to remove excessive slurry. Then, it was dried at 120°C for three hours and calcined at 500°C for one hour, thereby preparing each catalyst. The coating amount of the slurry was 150 g with respect to 1 liter of the honeycomb support.

Comparative Example 1

[0077] Gamma-alumina powder having a specific surface area of 150 m²/g was prepared as a catalyst support of Comparative Example 1, and platinum was loaded on the support in the same way as above. Then the obtained Pt-loaded powder was immersed in a barium acetate aqueous solution containing barium by 25 % by weight of that powder. After stirred for one hour, the solution was evaporated to dryness, thereby obtaining powder. After dried at 120°C for 12 hours, the powder was subjected to a thermal treatment at 500°C for one hour, thereby loading barium. The loading amount of barium was 25 % by weight.

[0078] This catalyst powder was made into slurry and coated on a honeycomb support in the same way as above, and subjected to a thermal treatment, thereby obtaining a catalyst.

Comparative Example 2

[0079] A catalyst support of Comparative Example 2 was prepared in the same way as that of Comparative Example 1, except that a cesium nitrate aqueous solution containing cesium by 25 % by weight of the Pt-loaded catalyst support powder, and made into a catalyst in the same way as in Comparative Example 1.

Examination and Evaluation

<Initial Conversion>

[0080] Each of the honeycomb catalysts of the examples of the present invention and the comparative examples was examined about the average conversions of CO, HC and NO_x by introducing lean model gas and stoichiometric model gas shown in Table 1 alternately for one minute each at gas hourly space velocity of 100,000 at inlet gas temperatures of 300°C, 400°C and 500°C. The results are shown in Table 2.

<Conversion After Durability Test>

[0081] Each of the honeycomb catalysts of the examples of the present invention and the comparative examples was subjected to a durability test in which the lean model gas shown in Table 1 for four minutes and the stoichiometric model gas shown in Table 1 for one minute were alternately introduced to the catalyst bed at an inlet gas temperature of 800°C for ten hours in total. Then each catalyst was examined about conversion after the durability test in the same way as the above initial conversion was examined.

[TABLE 1]

	CO %	C ₃ H ₈ ppm	CO ₂ %	O ₂ %	H ₂ O %	NO ppm	SO ₂ ppm	N ₂
LEAN MODEL GAS	0.1	800	12.0	4.5	10	1000	200	BALANCE
STOICHIOMETRIC MODEL GAS	0.75	800	10.0	VARIABLE	10	1000	200	BALANCE

(TABLE 2)

	METAL EXCEPT Al	MO. — Al ₂ O ₃	INLET GAS TEMP. 3 0 0 °C						INLET GAS TEMP. 4 0 0 °C						INLET GAS TEMP. 5 0 0 °C					
			INITIAL CONVERSION (%)			CONVERSION AFTER DURABILITY TEST (%)			INITIAL CONVERSION (%)			CONVERSION AFTER DURABILITY TEST (%)			INITIAL CONVERSION (%)			CONVERSION AFTER DURABILITY TEST (%)		
			CO	H C	NOx	CO	H C	NOx	CO	H C	NOx	CO	H C	NOx	CO	H C	NOx	CO	H C	NOx
EXAMPLES	1	C s	100	45	95	96	43	78	100	59	97	96	55	81	99	84	98	95	80	80
	2	C s	100	49	97	94	45	80	100	66	98	95	80	82	100	91	97	94	87	81
	3	C s	99	68	97	93	64	83	99	90	98	94	84	85	100	97	95	95	91	82
	4	C s	98	69	98	94	65	81	99	92	98	95	87	82	100	99	95	95	92	80
	5	C s	97	87	87	93	84	81	98	100	79	94	96	74	100	100	45	94	95	39
COMPARATIVE EXAMPLES	6	C s	100	39	76	60	29	45	100	54	80	65	43	48	100	79	79	65	64	46
	7	C s	96	95	56	93	81	37	98	100	41	94	89	31	99	100	12	94	90	3
EXAMPLES	8	Cs+Ca	97	89	91	93	83	86	99	99	93	95	94	89	100	100	90	95	95	87
	9	Cs+Ti	98	90	90	95	83	88	98	100	92	95	93	90	99	100	91	96	94	87
	10	Cs+K	98	90	94	95	83	87	99	100	96	96	92	88	100	100	95	96	93	86
	11	Cs+La	98	89	90	95	85	86	99	94	95	96	90	87	99	96	92	94	92	85
	C12	B a	97	98	98	94	91	78	98	99	76	95	92	43	98	99	11	94	92	2
COMPARATIVE EXAMPLES	1	B a	100	96	97	95	91	31	100	100	39	96	92	9	100	100	4	96	92	1
	2	C s	97	37	89	93	31	51	99	53	92	94	47	52	99	68	92	94	60	50

<Evaluation>

[0082] As apparent from Table 2, the catalysts of Comparative Examples C6 and C7 whose cesium contents were out of the range of claim 1 were deteriorated in initial NO_x conversion and NO_x conversion after the durability test.

5 [0083] Table 2 also demonstrates that the catalysts of Examples 8 to 11 in which a part of cesium was replaced with other metals were improved in NO_x conversion after the durability test than the catalysts of Examples 1 to 5 in which no part of cesium was replaced with other metals.

[0084] Further, in Comparative Examples 1 and 2, since alumina and each NO_x storage component did not constitute an amorphous composite oxide, there was a decrease in dispersability of the NO_x storage component, and as a result, Comparative Examples 1 and 2 were deteriorated in initial NO_x conversion and NO_x conversion after the durability test to Examples 12 and 2. The catalyst of Comparative Example C12 showed a sharp decrease in initial NO_x conversion and NO_x conversion after the durability test at the elevated inlet gas temperatures, although they were better than those of Comparative Example 1. This was because BaSO₄, which could not be easily decomposed, was generated due to sulfur poisoning. In the case where cesium was used with aluminum, however, even when the catalysts were poisoned by sulfur, generated sulfate could be easily decomposed at low temperatures, and produced little influence on NO_x conversion so that NO_x conversion after the durability test was less deteriorated.

(A Second Series of Preferred Embodiments Concerning a Method of Producing a Catalyst Support)

20 Comparative Example C13

[0085] An aqueous solution of alumina sol having a concentration of 10 % by weight and a specific surface area of 500 m²/g, an aqueous solution of barium hydroxide, water, and a small amount of acetic acid were mixed, and stirred at room temperature for five hours, while subjected to ultrasonic wave radiation.

25 [0086] This mixed sol solution was heated in a water bath at 80° C to be formed into gel, and dried at 120°C 4 for hours, thereby producing a catalyst support of Example C13. The molar ratio of barium to aluminum as oxides was BaO / Al₂O₃ = 1 / 3.

Comparative Example C14

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[0087] A catalyst support of Example C14 was produced in the same way as that of Example C13, except that the mixing ratio of alumina sol to barium hydroxide was controlled so that the molar ratio of barium to aluminum as oxides was BaO / Al₂O₃ = 1 / 6.

35 Comparative Example C15

[0088] A catalyst support of Example C15 was produced in the same way as that of Example C13, except that alumina sol having a concentration of 20 % by weight and a specific surface area of 500 m²/g was used, and that potassium nitrate was used instead of barium hydroxide. The molar ratio of potassium to aluminum as oxides was K₂O / Al₂O₃ = 1 / 6.

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Comparative Example C16

[0089] A catalyst support of Example C16 was produced in the same way as that of Example 15, except that the mixing ratio of potassium nitrate to alumina sol was controlled so that the molar ratio of potassium to aluminum as oxides was K₂O / Al₂O₃ = 1 / 11.

45

Example 17

50 [0090] A catalyst support of Example 17 was produced in the same way as that of Example C13 by employing the same alumina sol as in Example C13, except that cesium nitrate was used instead of barium hydroxide. The molar ratio of cesium to aluminum as oxides was Cs₂O / Al₂O₃ = 1 / 11.

Comparative Example C18

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[0091] A catalyst support of Example C18 was produced in the same way as that of Example C13 by employing the same alumina sol as in Example C13, except that lanthanum nitrate was used instead of barium hydroxide. The molar ratio of lanthanum to aluminum as oxides was La₂O₃ / Al₂O₃ = 1 / 3.

Comparative Example C19 C19.

[0092] Titania sol having a concentration of 10 % by weight and a specific surface area of 550 m²/g, barium hydroxide, water, and a small amount of acetic acid were mixed, and stirred at room temperature for five hours, while subjected to ultrasonic wave radiation.

[0093] This mixed sol solution was heated in a water bath at 80°C to be formed into gel, and dried at 120°C for four hours, thereby producing a catalyst support of Example C19. The molar ratio of barium to titanium as oxides was BaO / TiO₂ = 1 / 4.

Comparative Example C20

[0094] Silica sol having a concentration of 5 % by weight and a specific surface area of 600 m²/g, barium hydroxide, water, and a small amount of acetic acid were mixed and stirred at room temperature for five hours, while subjected to ultrasonic wave radiation. This mixed sol solution was heated in a water bath at 80°C to be formed into gel, and dried at 120°C for four hours, thereby producing a catalyst support of Example C20. The molar ratio of barium to silicon as oxides was BaO / SiO₂ = 3 / 5.

Comparative Example 3

[0095] Triisopropoxy aluminum and diisopropoxy barium were respectively weighed, and dissolved in 2-propanol at 80°C. This mixed solution was made into gel by a hydrolysis treatment. After the resulting gel was aged at 80°C for five hours, 2-propanol was recovered by vibration-fluidized drying. The obtained dried powder was calcined at 450°C, thereby preparing a catalyst support of Comparative Example 3. The molar ratio of barium to aluminum as oxides was BaO / Al₂O₃ = 1 / 3.

Comparative Example 4

[0096] A catalyst support of Comparative Example 4 was produced in the same way as that of Comparative Example 3, except that the mixing ratio of barium alkoxide to aluminum alkoxide was controlled so that the molar ratio of barium to aluminum as oxides was BaO / Al₂O₃ = 1 / 6.

Comparative Example 5

[0097] Activated alumina powder having a specific surface area of 200 m²/g, and barium acetate were weighed. Then the activated alumina powder was mixed in an aqueous solution of the barium acetate, whereby barium was loaded on activated alumina by impregnation at room temperature. Then, the entire material was dried and calcined at 500°C for five hours, thereby producing a catalyst support of Comparative Example 5. The molar ratio of barium to aluminum as oxides was BaO / Al₂O₃ = 1 / 3.

Comparative Example 6

[0098] A catalyst support of Comparative Example 6 was produced in the same way as that of Comparative Example 5, except that the mixing ratio of the respective powders was controlled so that the molar ratio of barium to aluminum as oxides was BaO / Al₂O₃ = 1 / 6.

Examination and Evaluation

[0099] The respective catalyst supports were respectively air calcined at temperatures shown in Table 3 for five hours. Then, their specific surface areas were measured, and the results are shown in Table 3. Besides, the crystal structure of the respective catalyst supports after the above calcination was investigated by an X-ray diffraction analysis, and the results are shown in Table 3. Table 3 also indicates a comparison in the production cost of the respective catalyst supports, when the production cost of the catalyst support of Comparative Example 3 is regarded as 1.

[0100] Table 3 shows that the catalyst support of example 17 of the present invention exhibited as high specific surface areas as 100 m²/g or more even when calcined at temperatures of 900°C or more, so, it was superior in heat resistance.

[0101] On the other hand, Table 3 also demonstrates that the catalyst supports of Comparative Examples 5 and 6 exhibited a remarkable decrease in specific surface area due to calcination, so, they were poor in heat resistance. This was because the catalyst supports of Comparative Examples 5 and 6 were not amorphous but crystalline.

[0102] Although the catalyst supports of Comparative Examples 3 and 4 possessed large specific surface areas, amorphous states, and superior heat resistance, their production costs were extremely higher than those of the examples of the present invention.

[TABLE 3]

					SPECIFIC SURFACE AREA (m ² /g)			CRYSTAL STRUCTURE	COST RATIO
					CALCINATION TEMP. (°C)				
					800	900	1000		
COMPARATIVE EXAMPLES	C13	ALUMINA SOL	Ba(OH) ₂	BaO/Al ₂ O ₃ =1/3	1 2 8	1 0 5	—	AMORPHOUS	0. 0 2
	C14	ALUMINA SOL	Ba(OH) ₂	BaO/Al ₂ O ₃ =1/6	1 6 3	1 2 0	1 0 7	AMORPHOUS	0. 0 1
	C15	ALUMINA SOL	KNO ₃	K ₂ O/Al ₂ O ₃ =1/6	1 3 4	—	1 0 2	AMORPHOUS	0. 0 5
	C16	ALUMINA SOL	KNO ₃	K ₂ O/Al ₂ O ₃ =1/11	1 4 6	—	1 0 1	AMORPHOUS	0. 0 2
EXAMPLE	17	ALUMINA SOL	CsNO ₃	Cs ₂ O/Al ₂ O ₃ =1/11	1 8 5	—	1 2 1	AMORPHOUS	0. 1 5
	C18	ALUMINA SOL	La(NO ₃) ₃	La ₂ O ₃ /Al ₂ O ₃ =1/3	—	—	1 0 0	AMORPHOUS	0. 0 5
COMPARATIVE EXAMPLES	C19	TITANIA SOL	Ba(OH) ₂	BaO/TiO ₂ =1/4	1 2 5	—	1 1 7	AMORPHOUS	0. 0 1
	C20	SILICA SOL	Ba(OH) ₂	BaO/SiO ₂ =3/5	1 1 2	—	1 0 3	AMORPHOUS	0. 0 1
	3	Al(OC ₂ H ₅) ₃	Ba(OC ₂ H ₅) ₂	BaO/Al ₂ O ₃ =1/3	1 3 2	—	1 1 1	AMORPHOUS	1. 0
	4	Al(OC ₂ H ₅) ₃	Ba(OC ₂ H ₅) ₂	BaO/Al ₂ O ₃ =1/6	—	—	1 2 4	AMORPHOUS	1. 0
	5	ACTIVATED ALUMINA	Ba(CH ₃ COO) ₂	BaO/Al ₂ O ₃ =1/3	7 6	—	3 2	CRYSTALLINE	0. 0 5
	6	ACTIVATED ALUMINA	Ba(CH ₃ COO) ₂	BaO/Al ₂ O ₃ =1/6	—	—	5 2	CRYSTALLINE	0. 0 2

(A Third Series of Preferred Embodiments Concerning a Catalyst and its Production Method)

Comparative Example C21

<First Step>

[0103] Aluminum alkoxide and barium alkoxide were weighed so that the molar ratio of aluminum to barium was $\text{Al}_2\text{O}_3 / \text{BaO} = 1 / 3$ when converted to oxides. Then the aluminum alkoxide and barium alkoxide were dissolved into propanol at 80°C, and acetyl alcohol as a hydrolysis inhibitor was added. Further, necessary water for hydrolysis was dropped, and the solution was aged at 80°C for five hours to obtain uniform gel. This gel was subjected to a vibration-fluidized drier and the solvent was recovered and the resulting material was ground to obtain dried power. This powder was calcined first at 450°C, and then at 900°C for five hours, thereby preparing catalyst support powder. The catalyst support powder after calcination was examined about crystal structure by an X-ray diffraction analysis, and about specific surface area.

<Second Step>

[0104] Cerium nitrate and zirconium nitrate were weighed so that the molar ratio of cerium to zirconium was $\text{CeO}_2 / \text{ZrO}_2 = 5 / 1$ when converted to oxides, and dissolved into distilled water at 60°C to prepare a mixed solution. Urea was added to this mixed solution to allow uniform precipitate. Then, the precipitate was recovered while washed with distilled water, dried at 120°C, and calcined at 900°C for five hours. The particle diameter of the powder after calcination was measured by microscopic observation, and the specific surface area of the powder after calcination was also measured.

[0105] After that, this powder was mixed in a predetermined amount of a platinum dinitrodiammine aqueous solution having a predetermined concentration. Then, after dried, the mixed solution was calcined at 250°C, thereby preparing Pt-loaded powder. The loading amount of platinum was 2 % by weight.

<Third Step>

[0106] 100 parts by weight of the above catalyst support powder, and 30 parts by weight of the above Pt-loaded powder, and 180 parts by weight of propanol were commingled to prepare slurry. A honeycomb monolith was immersed in this slurry. After pulled up and blown away to remove excessive slurry, the monolith was dried at 120°C and subjected to a thermal treatment at 500°C, thereby preparing a catalyst.

[0107] Supernatant liquid of the employed slurry was collected and examined about the eluting amount of barium. Further, the specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example C22

[0108] A catalyst of Example C22 was prepared in the same way as that of Example C21, except that aluminum alkoxide and barium alkoxide were employed so that the molar ratio of aluminum to barium was $\text{Al}_2\text{O}_3 / \text{BaO} = 1 / 6$ when converted to oxides, and that the calcination temperatures in the first step and the second step were 1000°C. Similarly, supernatant liquid of the employed slurry was collected and examined about the eluting amount of barium. The specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example C23

[0109] A catalyst of Example C23 prepared in the same way as that of Example C21, except that aluminum alkoxide and barium alkoxide were employed so that the molar ratio of aluminum to barium was $\text{Al}_2\text{O}_3 / \text{BaO} = 1 / 12$ when converted to oxides, and that the calcination temperatures in the first step and the second step were 1,000°C. Similarly, supernatant liquid of the employed slurry was collected and examined about the eluting amount of barium. Further, the specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example C24

[0110] A catalyst of Example C24 was prepared in the same way as that of Example C22, except that cerium nitrate

and zirconium nitrate were employed in the second step so that the molar ratio of cerium to zirconium was $\text{CeO}_2 / \text{ZrO}_2 = 3 / 1$ when converted to oxides. Similarly, supernatant liquid of the employed slurry was collected and examined about the eluting amount of barium. Further, the specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Example 25

[0111] A catalyst of Example 25 was prepared in the same way as that of Example C21, except that aluminum alkoxide and cesium alkoxide were employed so that the molar ratio of aluminum to cesium was $\text{Al}_2\text{O}_3 / \text{Cs}_2\text{O} = 1 / 6$ when converted to oxides, and that the calcination temperatures in the first step and the second step were 1000°C . Similarly, supernatant liquid of the employed slurry was collected and examined about the eluting amount of cesium. Further, the specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Example 26

[0112] A catalyst of Example 26 was prepared in the same way as that of Example C21, except that aluminum alkoxide and cesium alkoxide were employed so that the molar ratio of aluminum to cesium was $\text{Al}_2\text{O}_3 / \text{Cs}_2\text{O} = 1 / 11$ when converted to oxides, and that the calcination temperatures in the first step and the second step were 1000°C . Similarly, supernatant liquid of the employed slurry was collected and examined about the eluting amount of cesium. Further, the specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example C27

[0113] A catalyst of Example C27 was prepared in the same way as that of Example C21, except that aluminum alkoxide and lanthanum alkoxide were employed so that the molar ratio of aluminum to lanthanum was $\text{Al}_2\text{O}_3 / \text{La}_2\text{O}_3 = 1 / 3$ when converted to oxides, and that the calcination temperatures in the first step and the second step were $1,000^\circ\text{C}$. Similarly, supernatant liquid of the employed slurry was collected and measured about the eluting amount of lanthanum. The specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example C28

[0114] A catalyst of Example C28 was prepared in the same way as that of Example C21, except that aluminum alkoxide and lanthanum alkoxide were employed so that the molar ratio of aluminum to lanthanum was $\text{Al}_2\text{O}_3 / \text{La}_2\text{O}_3 = 1 / 6$ when converted to oxides, and that the calcination temperatures in the first step and the second step were $1,000^\circ\text{C}$. Similarly, supernatant liquid of the employed slurry was collected and examined about the eluting amount of lanthanum. Further, the specific surface area of the coating layer after the thermal treatment was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example 7

[0115] The catalyst support powder prepared in Example C21 and comprising a composite oxide of barium and aluminum was impregnated with a predetermined amount of a platinum dinitrodiammine aqueous solution having a predetermined concentration, and calcined at 250°C , thereby loading platinum. Supernatant liquid of the mixed solution of the catalyst support powder and the platinum dinitrodiammine aqueous solution was collected and examined about the eluting amount of barium. Further, the specific surface area of the coating layer after a thermal treatment at 800°C was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example 8

[0116] Catalyst support powder prepared in Example C22 and comprising a composite oxide of barium and aluminum was impregnated with a predetermined amount of a platinum dinitrodiammine aqueous solution having a predetermined concentration, and calcined at 250°C , thereby loading platinum. Supernatant liquid of the mixed solution of the catalyst support powder and the platinum dinitrodiammine aqueous solution was collected and examined about the eluting

amount of barium. Further, the specific surface area of the coating layer after a thermal treatment at 800°C was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

5 Comparative Example 9

10 [0117] Catalyst support powder prepared in Example C23 and comprising a composite oxide of barium and aluminum was impregnated with a predetermined amount of a platinum dinitrodiammine aqueous solution having a predetermined concentration, and calcined at 250°C, thereby loading platinum. Supernatant liquid of the mixed solution of the catalyst support powder and the platinum dinitrodiammine aqueous solution was collected and examined about the eluting amount of barium. The specific surface area of the coating layer after a thermal treatment at 800°C was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

15 Comparative Example 10

20 [0118] Catalyst support powder prepared in Example C21 and comprising a composite oxide of barium and aluminum was mixed with cerium oxide powder in which zirconium was solid solved at the same mixing ratio as in Example C21. The mixed powder was impregnated with a predetermined amount of a platinum dinitrodiammine aqueous solution having a predetermined concentration, and calcined at 250°C, thereby loading platinum. Supernatant liquid of the mixed solution of the catalyst support powder and the platinum dinitrodiammine aqueous solution was collected and examined about the eluting amount of barium. Further, the specific surface area of the coating layer after a thermal treatment at 800°C was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

25 Comparative Example 11

30 [0119] Catalyst support powder prepared in Example C22 and comprising a composite oxide of barium and aluminum was mixed with cerium oxide powder in which zirconium was solid solved at the same mixing ratio as in Example C22. This mixed powder was impregnated with a predetermined amount of a platinum dinitrodiammine aqueous solution having a predetermined concentration, and calcined at 250°C, thereby loading platinum. Supernatant liquid of the mixed solution of the catalyst support powder and the platinum dinitrodiammine aqueous solution was collected, and examined about the eluting amount of barium. The specific surface area of the coating layer after a thermal treatment at 800°C was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

Comparative Example 12

40 [0120] Catalyst support powder prepared in Example C23 and comprising a composite oxide of barium and aluminum was mixed with cerium oxide powder in which zirconium was solid solved at the same mixing ratio as in Example C23. This mixed powder was impregnated with a predetermined amount of a platinum dinitrodiammine aqueous solution having a predetermined concentration, and calcined at 250°C, thereby loading platinum. Supernatant liquid of the mixed solution of the catalyst support powder and the platinum dinitrodiammine aqueous solution was collected and examined about the eluting amount of barium. The specific surface area of the coating layer after a thermal treatment at 800°C was measured, and the composition of that coating layer was determined by an X-ray diffraction analysis. The results are shown in Table 4.

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[TABLE 4]

	COMPARATIVE EXAMPLES	CeO ₂ :ZrO ₂	Al ₂ O ₃ :BaO, Cs ₂ O, La ₂ O	CALCINATION TEMPERATURE	Pt-LOADED POWDER		CATALYST SUPPORT POWDER		ELUTION OF NO _x STORAGE COMPONENT	CONTAINING LAYER AFTER THERMAL TREATMENT		
					DIAH- ETER	SPECIFIC SURFACE AREA	SPECIFIC SURFACE AREA	CRYSTAL STRUCTURE		SPECIFIC SURFACE AREA	CRYSTAL STRUCTURE	
C21		5 : 1	1 : 3 - -	900 °C	82 Å	107 m ² /g	121 m ² /g	AMORPHOUS	0.1wt% OR LESS	112 m ² /g	AMORPHOUS	
C22		5 : 1	1 : 6 - -	1000 °C	82 Å	107 m ² /g	106 m ² /g	AMORPHOUS	0.1wt% OR LESS	105 m ² /g	AMORPHOUS	
C23		5 : 1	1 : 1 2 - -	1000 °C	82 Å	107 m ² /g	115 m ² /g	AMORPHOUS	0.1wt% OR LESS	108 m ² /g	AMORPHOUS	
C24		3 : 1	1 : 6 - -	900 °C	95 Å	102 m ² /g	106 m ² /g	AMORPHOUS	0.1wt% OR LESS	104 m ² /g	AMORPHOUS	
C25		5 : 1	1 : - 6 -	1000 °C	82 Å	107 m ² /g	108 m ² /g	AMORPHOUS	0.1wt% OR LESS	107 m ² /g	AMORPHOUS	
C26		5 : 1	1 : - 1 1 -	1000 °C	82 Å	107 m ² /g	119 m ² /g	AMORPHOUS	0.1wt% OR LESS	112 m ² /g	AMORPHOUS	
C27		5 : 1	1 : - - 3	1000 °C	82 Å	107 m ² /g	101 m ² /g	AMORPHOUS	0.1wt% OR LESS	103 m ² /g	AMORPHOUS	
C28		5 : 1	1 : - - 6	1000 °C	82 Å	107 m ² /g	117 m ² /g	AMORPHOUS	0.1wt% OR LESS	111 m ² /g	AMORPHOUS	
7		-	1 : 3 - -	900 °C	-	-	-	-	-	5.4 wt%	45 m ² /g	BaAl ₂ O ₄
8		-	1 : 6 - -	1000 °C	-	-	-	-	-	3.3 wt%	63 m ² /g	BaAl ₂ O ₄
9		-	1 : 1 2 - -	1000 °C	-	-	-	-	-	2.4 wt%	75 m ² /g	BaAl ₂ O ₄
10		5 : 1	1 : 3 - -	900 °C	-	-	-	-	-	3.5 wt%	68 m ² /g	BaAl ₂ O ₄
11	5 : 1	1 : 6 - -	1000 °C	-	-	-	-	-	2.1 wt%	69 m ² /g	BaAl ₂ O ₄	
12	5 : 1	1 : 1 2 - -	1000 °C	-	-	-	-	-	1.3 wt%	85 m ² /g	BaAl ₂ O ₄	

Evaluation

[0121] As apparent from Table 4, in the comparative examples, the elution of barium was observed, and after the thermal treatments, the reaction of barium and aluminum generated BaAl_2O_4 crystals, which caused a decrease in specific surface area. In the examples of the present invention, however, the elution of the NO_x storage components was not observed, and the amorphous state and high specific surface area was maintained even after the thermal treatments. Thus, the heat resistance was excellent.

(A Third Series of Preferred Embodiments Concerning a Catalyst using a Catalyst Support Using Cesium Oxide and Alumina)

Example 29

[0122] A predetermined amount of alumina powder was impregnated with a predetermined amount of a platinum dinitrodiammine nitrate aqueous solution, dried at 120°C , and calcined at 250°C , thereby obtaining Pt-loaded powder. The loading amount of platinum was 2 % by weight.

[0123] 50 parts by weight of catalyst support powder produced in the same way as that of Example 1 and comprising a Cs-Al composite oxide (specific surface area: $68 \text{ m}^2/\text{g}$, $\text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 = 1 / 4$) was mixed with 50 parts by weight of the above Pt-loaded powder, and propanol was added to the mixed powder to prepare uniform slurry. Then the slurry was coated on the same honeycomb support formed of cordierite as used in the first series of preferred embodiments. After dried at 120°C for three hours, the honeycomb support was calcined at 500°C for one hour to obtain a catalyst. The coating amount of the slurry was 150 g with respect to 1 liter of the honeycomb support.

[0124] Further, supernatant liquid of the above slurry was collected and the eluting amount of cesium was determined by chemical analysis. The result is shown in Table 5.

[0125] The obtained catalyst was examined about the loading amount of cesium, and conversions of HC and NO_x at two levels, that is, at the initial stage and after a thermal treatment at 800°C for ten hours. The results are also shown in Table 5.

Example 30

[0126] A catalyst of Example 30 was prepared in the same way as that of Example 29, except that 70 parts by weight of the catalyst support powder and 30 parts by weight of the Pt-loaded powder were mixed and made into slurry. The eluting amount of cesium and conversions of HC and NO_x were measured in the same way as in Example 29. The results are shown in Table 5.

Example 31

[0127] A catalyst of Example 31 was prepared in the same way as that of Example 29, except that 90 parts by weight of the catalyst support powder and 10 parts by weight of the Pt-loaded powder were mixed and made into slurry. The eluting amount of cesium and conversions of HC and NO_x were measured in the same way as in Example 29. The results are shown in Table 5.

Comparative Example 13

[0128] A predetermined amount of the same catalyst support powder as used in Example 29 was impregnated with a predetermined amount of a platinum dinitrodiammine nitrate aqueous solution having a predetermined concentration. After dried at 120°C , the resulting powder was calcined at 250°C to obtain catalyst powder. The loading amount of platinum was 1.5 % by weight.

[0129] A catalyst of Comparative Example 13 was prepared in the same way as that of Example 29, except that slurry was prepared by using this catalyst powder. Further, the eluting amount of cesium and conversions of HC and NO_x were measured in the same way as in Example 29. The results are shown in Table 5.

Comparative Example 14

[0130] Pt-loaded powder was prepared in the same way as in Example 29, except that the loading amount of platinum was 1.5 % by weight. The Pt-loaded powder was impregnated with a predetermined amount of a cesium acetate aqueous solution having a predetermined concentration. After dried at 120°C , the resulting powder was calcined at 500°C for one hour, thereby loading cesium. The loading amount of cesium was 0.3 mol with respect to 120 g of alumina.

[0131] A catalyst of Comparative Example 14 was prepared in the same way as that of Example 29, except that slurry was prepared by employing the obtained Pt-Cs loaded powder. The eluting amount of cesium and conversions of HC and NO_x were measured in the same way as in Example 29. The results are shown in Table 5.

[TABLE 5]

	Cs (WT %)			HC CONVERSION		NO _x CONVERSION	
	SUPERNATANT LIQUID	INITIAL	AFTER THERMAL TREATMENT	INITIAL	AFTER THERMAL TREATMENT	INITIAL	AFTER THERMAL TREATMENT
EX. 29	0.1 >	11.0	10.8	98	99	86	82
EX. 30	0.1 >	15.2	14.9	96	98	93	81
EX. 31	0.1 >	19.4	19.0	95	98	94	80
COM. EX. 13	2.1	19.1	11.4	67	71	93	46
COM. EX. 14	3.4	24.5	8.1	63	70	84	34

Evaluation

[0132] As seen from Table 5, in the catalysts of the examples of the present invention, the eluting amounts of cesium were remarkably small, and the loading amounts of cesium were hardly decreased by the thermal treatments. On the other hand, in the catalysts of the comparative examples, the eluting amounts of cesium were large. Particularly in the catalyst of Comparative Example 14, the thermal treatment brought a sharp decrease in the loading amount of cesium.

[0133] The catalysts of the examples of the present invention exhibited high conversions of HC and NO_x both at the initial stage and after the thermal treatments. On the other hand, the catalysts of the comparative examples exhibited low HC conversion at the initial stage and remarkably decreased NO_x conversion after the thermal treatments.

[0134] In the comparative examples, it is supposed that when the powder was impregnated with the platinum aqueous solution or made into slurry, cesium was eluted, which caused a decrease in the dispersability of cesium, and accordingly cesium flew away hard at the time of the thermal treatments. Particularly in Comparative Example 14, because the cesium dispersability was particularly low, the flying away of cesium was especially hard, and as a result, the NO_x storage ability after the thermal treatment was largely decreased. Further, in the comparative examples, since platinum was loaded in the vicinity of cesium, the oxidation force of platinum was decreased, and therefore HC conversion was low even at the initial stage.

[0135] On the other hand, in the catalysts of the examples of the present invention, because cesium was highly dispersed and not in contact with the platinum aqueous solution, the elution and aggregation of cesium was extremely small, so NO_x conversion was maintained high even after the thermal treatments. Further, since cesium was loaded at some distance from platinum, oxidation force of platinum was prevented from decreasing, which achieved high HC conversion.

Claims

1. A high heat-resistant catalyst support comprising:

alumina, and

an NO_x storage component consisting of cesium oxide, wherein a part of said cesium oxide in the following formula (1) may be replaced with an oxide of at least one element selected from the group consisting of alkali metals except cesium, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper,

said alumina and said NO_x storage component constituting an amorphous composite oxide,

wherein said alumina and said NO_x storage component have a molar ratio satisfying the following formula (1) :

$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1 / 90 \quad (1),$$

and

said amorphous composite oxide is an amorphous composition which has been subjected to a thermal treatment at a temperature at which said composition is not crystallized.

2. A method of producing the high heat-resistant catalyst support of claim 1, comprising the steps of:

mixing a solution of a cesium compound which may include one further element selected from the group consisting of alkali metals, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper, with a solution of alumina sol to prepare a mixed sol solution,

forming said mixed sol solution into gel, and

drying and calcining said gel.

3. A high heat-resistant catalyst comprising:

a high heat-resistant catalyst support comprising an amorphous composition comprising alumina and an NO_x storage component consisting of cesium oxide, wherein a part of said cesium oxide in the following formula (1) may be replaced with an oxide of at least one element selected from the group consisting of alkali metals except cesium, alkaline-earth metals, rare-earth elements except lanthanum and transition elements except copper, in which cesium oxide and alumina have a molar ratio satisfying the following formula (1):

$$1 / 3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1 / 90 \quad (1),$$

and which has been subjected to a thermal treatment at a temperature at which said composition is not crystallized; and

a porous support loaded with a noble metal.

Patentansprüche

1. Ein gegenüber großer Hitze beständiger Katalysatorträger, welcher umfaßt:

Aluminiumoxid, und

eine NO_x-speichernde Komponente, die aus Cäsiumoxid besteht, worin ein Teil des Cäsiumoxids der folgenden Formel (1) durch ein Oxid von wenigstens einem Element aus der Gruppe: Alkalimetalle mit Ausnahme von Cäsium, Erdalkalimetalle, seltene Erde-Elemente außer Lanthan und Übergangselemente außer Kupfer ersetzt sein kann, und

dieses Aluminiumoxid und diese NO_x-speichernde Komponente ein amorphes Mischoxid bilden,

wobei das Aluminiumoxid und die NO_x-speichernde Komponente ein Molverhältnis entsprechend der folgenden Formel (1) aufweisen:

$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1 / 90 \quad (1),$$

und

dieses amorphe Mischoxid eine amorphe Zusammensetzung ist, die einer thermischen Behandlung bei einer Temperatur unterworfen worden ist, bei der diese Zusammensetzung nicht kristallisiert ist.

2. Verfahren zur Herstellung eines gegenüber großer Hitze beständigen Katalysatorträgers nach Anspruch 1 mit den Stufen:

Vermischen einer Lösung einer Cäsiumverbindung, welche ein weiteres Element aus der Gruppe: Alkalimetalle, Erdalkalimetalle, seltene Erde-Elemente außer Lanthan und Übergangselemente außer Kupfer enthalten kann, mit einer Lösung von Aluminiumoxidsol, um eine gemischte Sollösung herzustellen,

Überführung dieser gemischten Sollösung in ein Gel, und

Trocknen und Calcinieren dieses Gels.

3. Ein gegenüber großer Hitze beständiger Katalysator, welcher umfaßt:

einen gegenüber großer Hitze beständigen Katalysatorträger, der eine amorphe Zusammensetzung mit Aluminiumoxid und einer NO_x-speichernden Komponente umfaßt, die aus Cäsiumoxid besteht, worin ein Teil dieses Cäsiumoxids in der folgenden Formel (1) durch ein Oxid von wenigstens einem Element aus der Gruppe: Alkalimetalle mit Ausnahme von Cäsium, Erdalkalimetalle, seltene Erde-Elemente außer Lanthan und Übergangselemente außer Kupfer ersetzt sein kann, in welcher Cäsiumoxid und Aluminiumoxid ein Molverhältnis entsprechend der folgenden Formel (1) aufweisen:

$$1 / 3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1 / 90 \quad (1),$$

wobei dieser einer Wärmebehandlung bei einer Temperatur, bei der die genannte Zusammensetzung nicht kristallisiert ist, unterworfen worden ist, und der poröse Träger mit einem Edelmetall beladen ist.

Revendications

1. Un support de catalyseur résistant aux fortes chaleurs, comprenant :

de l'alumine, et

un composant de stockage de NO_x constitué d'oxyde de césium, dans lequel une partie dudit oxyde de césium dans la formule (1) suivante peut être remplacée par un oxyde d'au moins un élément choisi dans le groupe constitué par les métaux alcalins à l'exception du césium, les métaux alcalino-terreux, les éléments des terres rares à l'exception du lanthane et les éléments de transition à l'exception du cuivre, ladite alumine et ledit composant de stockage de NO_x constituant un oxyde composite amorphe, dans lequel ladite alumine et ledit composant de stockage de NO_x ont un rapport molaire satisfaisant à la formule (1) suivante :

$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1 / 90 \quad (1),$$

et

ledit oxyde composite amorphe est une composition amorphe qui a été soumise à un traitement thermique à

une température à laquelle ladite composition n'est pas cristallisée.

2. Un procédé de production du support de catalyseur résistant aux fortes chaleurs de la revendication 1, comprenant les étapes consistant à :

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mélanger une solution d'un composé du césium qui peut comprendre un autre élément choisi dans le groupe constitué par les métaux alcalins, les métaux alcalino-terreux, et les éléments des terres rares à l'exception du lanthane et les éléments de transition à (exception du cuivre, avec une solution de sol d'alumine pour

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préparer une solution de sol mixte, mettre ladite solution de sol mixte sous la forme d'un gel, et sécher et calciner ledit gel.

3. Un catalyseur résistant aux fortes chaleurs comprenant :

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un support de catalyseur résistant aux fortes chaleurs comprenant une composition amorphe comprenant de l'alumine et un composant de stockage de NO_x constitué d'oxyde de césium, dans lequel une partie dudit oxyde de césium dans la formule (1) suivante peut être remplacée par un oxyde d'au moins un élément choisi dans le groupe constitué par les métaux alcalins à l'exception du césium, les métaux alcalino-terreux, et les éléments des terres rares à l'exception du lanthane et les éléments de transition à l'exception du cuivre, où l'oxyde de césium et l'alumine ont un rapport molaire satisfaisant à la formule (1) suivante :

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$$1/3 > \text{Cs}_2\text{O} / \text{Al}_2\text{O}_3 > 1 / 90 \quad (1),$$

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et

et qui a été soumise à un traitement thermique à une température à laquelle ladite composition n'est pas cristallisée ; et

un support poreux chargé d'un métal noble.

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